

**CATALYST FOR ISOMERIZATION OF WAX, ISOMERIZING METHOD OF WAX,  
AND PRODUCTION OF LUBRICANT BASE OIL****Publication number:** JP8001008**Publication date:** 1996-01-09**Inventor:** ARIMA YOSHIO**Applicant:** JAPAN ENERGY CORP**Classification:**

**- international:** *B01J29/076; C10G45/12; C10G45/64; B01J29/00;  
C10G45/02; C10G45/58; (IPC1-7): B01J29/076;  
C10G45/12; C10G45/64*

**- european:****Application number:** JP19940163342 19940623**Priority number(s):** JP19940163342 19940623**Report a data error here****Abstract of JP8001008**

**PURPOSE:**To obtain a lubricant base oil at high yield by depositing at least one metal component selected from VIII group elements and VI-A group elements on a carrier prepared by mixing alumina with a specified amt. of crystalline molecular sieve having specified pore size and specified molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. **CONSTITUTION:**A carrier is obtd. by mixing alumina and crystalline molecular sieve having 6.5 to 7.5Angstrom major diameter of the pore size and  $\geq 50$  molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> by about 1-30 wt.%. Then at least one kind of metal component selected from VIII group metals and VI-A group elements in the periodical table is deposited on the carrier to obtain a catalyst. Then the obtd. catalyst is brought into contact with wax-base hydrocarbon oil containing  $\geq 50$ wt.% paraffin under pressurized hydrogen to isomerize the wax. Or, the intermediate of a lubricant base oil and slack wax are alternately passed through a reaction chamber filled with the catalyst so that hydrogenation refining of the intermediate of the lubricant oil and isomerization of the slack wax are alternately performed to produce a lubricant base oil.

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**CLAIMS**

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(57) [Claim(s)]

[Claim 1] The catalyst for wax isomerization which consists of having made at least one sort of metal components chosen as an alumina from nickel, cobalt, molybdenum, and a tungsten by the support which has pore with a major axis of 6.5-7.5A, and mixed the crystalline molecular sieve whose SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> mole ratio is 50 or more one to 30% of the weight support.

[Claim 2] The catalyst for wax isomerization characterized by a crystalline molecular sieve according to claim 1 being at least one chosen from Zeolite L, Zeolite omega, mordenite, or a silicoaluminophosphate molecular sieve.

[Claim 3] The isomerization approach of the wax characterized by contacting the wax system hydrocarbon oil which contains paraffin 50% of the weight or more for the catalyst for wax isomerization according to claim 1 under hydrogen pressurization.

[Claim 4] The isomerization approach of the wax characterized by a wax system hydrocarbon oil according to claim 3 being slack wax.

[Claim 5] The manufacture approach of the lubrication base oil which carries out the run of lubrication base oil manufacture intermediate field and the slack wax to the reactor filled up with the wax isomerization catalyst according to claim 1 by turns, and is characterized by performing hydrotreating of said lubrication base oil manufacture intermediate field, and isomerization of slack wax by turns.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention isomerizes a wax system hydrocarbon oil, especially slack wax, and relates the catalyst suitable for manufacturing the lubrication base oil which has a high viscosity index, and its catalyst to the isomerization approach of a \*\*\*\* wax, and a pan at the manufacture approach of lubrication base oil.

[0002]

[Description of the Prior Art] By isomerizing slack wax or performing alternative hydrocracking, lubrication base oil with a high viscosity index can be manufactured, and many things are proposed about an approach or a catalyst for it etc. Among these, the approach using fireproof oxide and the catalyst which specifically made the alumina support and supported nickel and/or cobalt, molybdenum and/or a tungsten, and the phosphorylation object to this as the manufacture approach of a lubricating oil of having a high viscosity index is proposed (JP,54-2204,B). However, by the approach using this catalyst, there was a fault that the conversion of isomerization was low and only low lubrication base oil yield was obtained.

[0003] For this reason, in order to raise conversion and to raise the yield of lubrication base oil, the approach using various catalysts is proposed.

[0004] For example, the catalyst (JP,62-112691,A, JP,5-504597,A, JP,4-226593,A) which supported hydrogenation / dehydrogenation components, such as palladium and platinum, on the subacidity zeolite (the zeolite beta which contains boron in a frame) with which an atmospheric-air hole zeolite (ZSM-5, 22, 23, 35) or an alpha value does not exceed 20, the catalyst (JP,62-25195,A, JP,4-503371,A) which supported platinum and palladium to the silicoaluminophosphate molecular sieve with an in-between pore aperture are shown.

[0005] Moreover, the catalyst (JP,60-133089,A) which supported platinum etc. to the refractory metal oxide support processed by the catalyst (JP,1-223196,A) which supported platinum etc. to the fluorinated refractory metal oxide support, tetra-ammonium aluminates, etc. is indicated.

[0006] However, the lubrication base oil obtained using this kind of catalyst may not yet be enough to use it as fuel-efficient mold motor oil in respect of the pour point or a viscosity index, further, the noble metals with low resistance to sulfur and nitrogen are used as an activity support metal, and most of these catalysts had the fault that the sulfur in a raw material and nitrogen content had to be controlled strictly. Therefore, in order to manufacture the base oil which isomerizes a wax etc. using the catalyst with which these noble metals were supported, and has a high viscosity index, another reactor for desulfurization and denitrification is needed.

[0007] Furthermore, it has the fault that the catalyst using a zeolite, a silicoaluminophosphate molecular sieve, etc. is expensive compared with an alumina support catalyst. Moreover, in order for the production process of a catalyst to become complicated and to use harmful reagents, such as a fluorine, for what processed refractory metal oxide support by the fluorine, tetra-ammonium aluminates, etc., it also had problems, such as safety reservation on manufacture.

[0008]

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned technical problem, and the purpose of this invention can prepare it by the simple approach. The resistance over sulfur and nitrogen uses the high, high wax isomerization catalyst of versatility, and its catalyst. It is in providing the isomerization approach of a wax of obtaining the lubrication base oil which has a high viscosity index called 140 or more and the low pour point by high yield, and a list with the manufacture approach of lubrication base oil that purification of the usual lubricating oil raw material and manufacture of the lubricating oil of the hyperviscous characteristic from slack wax can be performed by turns.

[0009]

[Means for Solving the Problem] In order to advance isomerization promptly on the dual function nature catalyst which supported the metal on fireproof oxide support, it is supposed that metaled dehydrogenation and hydrogenation activity, and the acidity (acidity per surface area) of support must be raised with both sufficient balance. For example, if a zeolite is used as support in order to raise acidity, a decomposition reaction will have priority and the base oil of a low viscosity index will be obtained only with low yield. Alternative decomposition and alternative isomerization are performed or the approach using what raised the  $\text{SiO}_2/\text{aluminum}_2\text{O}_3$  ratio of a crystalline molecular sieve using the molecular sieve effect using the crystalline molecular sieve which has a specific pole diameter as a policy for controlling this decomposition activity, and made acidity low etc. is learned. Moreover, the noble metals which have a dehydrogenation and hydrogenation activity high as a support metal, especially platinum were fond, and have been used in order to raise a dehydrogenation and hydrogenation activity. It is because it is supposed that this has indispensable noble-metals components, such as platinum, in the balance of metaled dehydrogenation and hydrogenation activity, and support acidity when a crystalline molecular sieve is made into a subject, and restricting is desirable as for use of base metal, such as nickel, (for example, ACS preprint 38(4) 788, 1993 reference).

[0010] However, the molecular sieve function was demonstrated enough, and having carried out little addition of the crystalline molecular sieve also unexpectedly at the alumina also found out that, as for the acidity, the acidity of a crystalline molecular sieve was reflected in the acidity of support as it is. And the support which added to the alumina the crystalline molecular sieve which has a specific pole diameter, and raised the  $\text{SiO}_2/\text{aluminum}_2\text{O}_3$  ratio more than fixed, and made acidity low Even if it supports 8 group base metal and 6A group metal which are used with general hydrorefining catalysts other than the metal which has very high hydrogenation ability like noble metals like palladium or platinum It found out that a dehydrogenation and hydrogenation activity, and the acidity of support balanced well, and isomerization of a wax advanced promptly.

[0011] This invention is what was made based on this knowledge. This invention to an alumina To the support which has pore with a major axis of 6.5-7.5Å, and mixed the crystalline molecular sieve whose  $\text{SiO}_2/\text{aluminum}_2\text{O}_4$  mole ratio is 50 or more one to 30% of the weight Nickel, cobalt, molybdenum, the catalyst for wax isomerization that consists of having made at least one sort of metal components chosen from a tungsten support, And the isomerization approach of the wax which consists of contacting the wax system hydrocarbon oil which contains paraffin 50% of the weight or more for the aforementioned catalyst for wax isomerization under hydrogen pressurization, It is the manufacture approach of the lubrication base oil which consists of carrying out the run of lubrication base oil manufacture intermediate field and the slack wax to the reactor which filled up the list with said wax isomerization catalyst by turns, and performing hydrorefining of said lubrication base oil manufacture intermediate field, and isomerization of slack wax by turns.

[0012] Although hydrated alumina is included in the alumina used for above-mentioned this invention, if it is the alumina usually used as support of a catalyst, or hydrated alumina as this alumina, especially trouble does not have anythings and they can be used.

[0013] The crystalline molecular sieve used for this invention needs to be the crystalline molecular sieve whose pore major axis is 6.5-7.5Å. If a pore major axis is smaller than 6.5Å, only decomposition of straight chain-like paraffin and the small branching paraffin of extent of branching will advance, and

isomerization will not advance. in this case, also although kicked, in order for components other than paraffin to make abundant \*\* rare \*\*\*\*\* and the so-called waxy distillate only form into the low pour point, when [ which used the wax as the raw material ] suitable, in the dewaxing processing performed succeedingly, the yield of lubrication base oil becomes remarkably low. On the other hand, if a pore major axis is larger than 7.5A, a molecular sieve function will be substantially lost to a wax, and only the base oil of low lubrication base oil fraction yield and a low viscosity index will be obtained.

[0014] The silicoaluminophosphate molecular sieve (SAPO) which are Zeolites L, Y, and omega, mordenite, and the zeolite analogue is mentioned to the crystalline molecular sieve whose pore major axis is 6.5-7.5A, and each of these can be used for it. However, although it has the pore whose pole diameter is 7.4A, since Zeolite Y has the-like secondary decomposition resulting from the channel structure, it is not [ among these ] so desirable to wax isomerization.

[0015] Moreover, this crystalline molecular sieve needs to make acidity low, and uses what made the SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> mole ratio 50 or more for this reason. catalyst deactivation according [ if SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> mole ratio does not fulfill 50, even if it is little addition, decomposition activity will be too high and only the base oil of low lubrication base oil fraction yield and a low viscosity index will be obtained or ] to deposition of Cork etc. -- intense -- a catalyst life -- short -- \*\*\*\* -- \*\*

[0016] Although especially the configuration of a crystalline molecular sieve is not asked, it is desirable to use 100 micrometers or less of things which have the median size of 0.1-50 micrometers preferably. Moreover, the addition to the alumina of a crystalline molecular sieve is made into 1 - 30wt%. When not filling the addition of a crystalline molecular sieve to 1wt%, isomerization activity is low and the addition exceeding 30wt% is because decomposition activity becomes high and isomerization selectivity becomes low. Even if the molecular sieve function of a crystalline molecular sieve and acidity are little addition, they are enough demonstrated in this amount. moreover, the addition of the crystalline molecular sieve to an alumina is comparatively little in this way -- as a hydrogenation metal component -- the [ the 8th group base metal and ] -- use of 6A group metal is enabled.

[0017] the [ the 8th group base metal of a periodic table which is used for a general hydrorefining catalyst as a support metal and which is a hydrogenation metal component, and ] -- it uses combining any one sort, such as 6A group metal, for example, nickel, cobalt, molybdenum, and a tungsten, or two sorts or more. These amounts of metal support are good to be the total quantity as a metal component and to select suitably in 10 - 20% of the weight of the range especially preferably to a catalyst, three to 30% of the weight. When a crystalline molecular sieve like a zeolite as catalyst support was used, in order to have made the acidity, and the dehydrogenation and hydrogenation activity ability of a hydrogenation metal component balance well generally, it was thought that the noble metals which have high hydrogenation ability were required. However, in the support which carried out little addition of the crystalline molecular sieve with 1 - 30 % of the weight at the alumina, if the molecular sieve has suitable pore structure and acidity, the acidity as the whole support can be weakened moderately, consequently even if it is base metal, isomerization will advance promptly.

[0018] In addition, it may combine with these metal components and elements other than this, for example, Lynn etc., may be supported. Other elements, such as Lynn, are good to select suitably in 1 - 7% of the weight of the range.

[0019] The catalyst of this invention is the following, and can be made and prepared.

[0020] First, although an alumina and a crystalline molecular sieve are mixed and kneaded, even if this mixes both before kneading, kneading an alumina, it may add and mix and it may use a crystalline molecular sieve. it is not necessary to perform a special thing in this mixing, and it is only mixed mechanically -- being sufficient . In this kneading, it is desirable to use a nitric-acid solution as a deflocculant 1 to 5%. Moreover, which a well-known kneading machine can be used in kneading. After kneading is good to fabricate using an extruding press machine etc. As for the configuration in this case, it is desirable to fabricate in consideration of a cylinder form, 3 leaf shapes, and the reactor that it spherical-\*\* and is used, and it is good to make it have the maximum cross-section diameter which are 1 / 16 - 1/32 inch.

[0021] next, this moldings -- the temperature of 50-200 degrees C -- 5 - 24 hours -- drying -- the

temperature of 250-800 degrees C -- it is 400-700 degrees C in temperature preferably, and calcinates in 1 - 2-hour air. thus, the metal component described above by the sinking-in method etc. to the obtained fireproof oxide support -- supporting -- the temperature of 50-200 degrees C -- 5 - 24 hours -- drying -- the temperature of 250-700 degrees C -- it is 400-600 degrees C in temperature preferably, and calcinates in 0.5 - 2-hour air.

[0022] The catalyst of this invention obtained as mentioned above is suitably used, in order to isomerize the wax system hydrocarbon oil which contains paraffin 50% of the weight or more as a raw material. The slack wax which is missing from solvent dewaxing equipment and is obtained is used suitably, without carrying out furfural solvent extraction processing, and processing the deasphalting processing oil for quality, a heavy fraction, or reduced pressure residue with hydrorefining equipment subsequently among the slack wax obtained at the solvent dewaxing process which is one of the lubricating oil production processes, i.e., reduced pressure, or processing especially as a wax system hydrocarbon oil which contains this paraffin 50% of the weight or more, although that class is not asked. These waxes may be independently processed for every fraction, and it may mix with the thing of other fractions and they may be used.

[0023] It is desirable for any method of the fixed bed, the moving bed, and the fluid bed to be able to perform this isomerization, and to carry out by the reaction condition of the temperature which is 300-400 degrees C, the hydrogen pressure which is 50-150kg/cm<sup>2</sup>, the hydrogen / wax ratio of 500 - 3000 l/l, and the liquid space velocity (LHSV) of 0.2-5.0hr-1.

[0024] In order to obtain the lubrication base oil of a high viscosity index with high yield, it is desirable to set up a reaction condition so that the invert ratio to the light fraction in which the invert ratio of straight chain-like paraffin has the boiling point below the initial boiling point of a raw material 90% or more may become 40 or less % of the weight. When a straight chain-like paraffin invert ratio does not reach to 90%, although a high viscosity index is expectable, the yield of lubrication base oil may fall in the dewaxing processing performed succeedingly, and it may not be able to make low enough the pour point of the lubrication base oil concerned. Moreover, if the inversion to a light part exceeds 40 % of the weight, a high viscosity index cannot be maintained the top where the yield of a lubrication base oil fraction is low, and it is not desirable.

[0025] Since the light fraction which is not desirable as lubrication base oil is contained in the generation oil obtained by this isomerization, distillation etc. separates this. It is desirable to perform this distillation under reduced pressure, and it is good to obtain residue which removes the fraction of 350 degrees C or less of boiling points, and has the 330-370-degree C initial boiling point.

[0026] After distilling an isomerization product, it can consider as lubrication base oil by applying to dewaxing equipment. The solvent dewaxing currently generally performed is sufficient as dewaxing in this case, for example, it is good to be a solvent / dewaxing raw material ratio 2 / the range of 1 - 4/1, and to carry out under -20--30 degree C temperature using the partially aromatic solvent (for example, 1 / 1 solvent ratio) of a methyl ethyl ketone/toluene.

[0027] Since at least one sort chosen from the nickel which is the hydrogenation metal component which is used for a hydrorefining catalyst general as a support metal, cobalt, molybdenum, and a tungsten is used for the above-mentioned catalyst, it also has hydrorefining functions, such as desulfurization and denitrification, with isomerization. Therefore, the vacuum distillation fraction of mineral oil etc. can also carry out hydrorefining of the manufacture intermediate field of usual lubrication base oil using this catalyst. Therefore, conventionally, isomerization and hydrorefining are one reactor by using this catalyst, although the separate reactor was performing, and can perform isomerization by turns with hydrorefining, respectively by letting usual lubrication base oil manufacture intermediate field and a usual wax pass by turns.

[0028] these two or more sorts of mixture, such as a raffinate which the above-mentioned usual lubrication base oil manufacture intermediate field are intermediate field generally obtained by the lubrication base oil production process, and carried out solvent refining of the propane deasphalting processing oil of a vacuum distillation fraction and the vacuum distillation residue, or these using the furfural typically and/or an oil which carried out solvent dewaxing, or an oil which carried out contact

dewaxing, etc. -- it is -- a sulfur content -- about 0.5-5wt% -- it is desirable to use what is contained.

[0029] This hydrorefining is good under 50-150kg/cm<sup>2</sup> hydrogen pressurization to carry out to the bottom of a condition with the hydrogen / oil ratio of 100 - 2000 l/l, a liquid space velocity [ of 0.5-5hr<sup>-1</sup> ] (LHSV), and a temperature of 250-400 degrees C.

[0030] Moreover, since the stock oil kind supplied to a reactor is changed, and conditions are reset up after that or conditions are reset up in case the above-mentioned hydrorefining and isomerization are performed by turns, you may carry out by which approach of changing a stock oil kind after that.

Although the lubrication base oil which has the target description isomerization from hydrorefining or since the activity of a catalyst is not fully demonstrated [ in / conversely / the early stages of the change to hydrorefining from isomerization ] cannot be obtained, activity can revive within a short period of time comparatively, and the lubrication base oil which has the target description can be obtained now.

[0031] In addition, although it is necessary to perform vacuum distillation in order for isomerization and the inversion to the light fraction by the decomposition reaction which is side reaction similarly to take place and for this hydrorefining to also remove the light fraction which is not desirable as this lubrication base oil, in hydrorefining and both of isomerization, a common fractionating tower can be used also about this distillation. Furthermore, although it may usually be applied to dewaxing equipment like [ after this hydrorefining ] the isomerization back, since this dewaxing condition does not have a difference so much in both, either, it can be used in common.

[0032] Moreover, although based also on the class of lubrication base oil manufacture intermediate field used in this hydrorefining, generally with a viscosity index of 120 or less lubrication base oil is obtained.

[0033]

[Example]

(Example 1)

1564g of preparation alumina powder of a catalyst was put into the kneading machine, nitric-acid water-solution 1 l of 3% concentration was added as a deflocculant, and it kneaded for 30 minutes, and mordenite (zeolite pore major-axis [ of 7.0Å ], mole ratio of SiO<sub>2</sub>/aluminum 2O<sub>3</sub> = 210) 117.7g of marketing was added to this, and it kneaded for 30 more minutes to it. This kneading object was fabricated with the extruding press machine which has the dice of the hole of 1.4mmphi in the shape of a cylinder, and it dried at 130 degrees C overnight. The dry matter was calcinated at 600 degrees C for 1 hour using rotary kiln, and catalyst support was obtained.

[0034] Molybdenum, nickel, and Lynn were sunk in using the sinking-in liquid which contains 46.5g of ammonium molybdates, 41.8g of nickel nitrate 6 hydrates, and 19.6g of phosphoric-acid solutions in 150g of this support. After drying this at 130 degrees C overnight, it calcinated for 30 minutes at 500 degrees C using rotary kiln, and Catalyst A was acquired.

[0035] After filling up the reaction container of a fixed-bed circulation type with the catalyst A acquired by the isomerization above of a wax and sulfurating this catalyst, it isomerized by circulating the heavy slack wax (13 % of the weight of oil, consistency 0.84 g/cm<sup>3</sup>, 330-600 degrees C of boiling ranges) obtained by carrying out solvent dewaxing of the heavy lubrication fraction after vacuum distillation to this. The reaction condition set to 80kg/cm<sup>2</sup> of hydrogen pressure, hydrogen / wax ratio 1500 l/l, and LHSV0.5hr<sup>-1</sup>, and temperature was changed among 350-380 degrees C. The gas chromatography analyzed the obtained generation oil and the result was shown in Table 1. In addition, NP invert ratio and the yield of a fraction with the boiling point lower than 330 degrees C were expressed for the percentage reduction of straight chain-like paraffin as cracking severity.

[0036]

[Table 1]

反応温度(℃)	3 5 0	3 6 1	3 6 5	3 7 0
NP転化率(%)	6 8 . 2	9 2 . 3	9 6 . 1	1 0 0
分解率(重量%)	1 4 . 0	3 2 . 3	4 4 . 8	6 7 . 6



[0037] (Examples 1-3 of a comparison)

It replaces with mordenite in an example 1, and is PQ. The zeolite beta (the zeolite pore major axis of 7.6Å, the mole ratio of SiO<sub>2</sub>/aluminum 2O<sub>3</sub> = 141) which carried out dealuminization of Silicalite made from Zeolite (the zeolite pore major axis of 5.6Å, the mole ratio of SiO<sub>2</sub>/aluminum 2O<sub>3</sub> = 250) and the commercial zeolite beta was used, respectively, and also Catalysts B and C were prepared by the same approach as an example 1. Moreover, Catalyst D was prepared by the same approach as an example 1 using the support of only an alumina, without adding mordenite. After sulfurating these catalysts, the isomerization experiment was conducted by the same approach as an example 1 except reaction temperature having been shown in Table 2. These results were shown in Table 2.

[0038]

[Table 2]

触媒	B	C	D
反応温度(℃)	335	337	400
NP転化率(%)	93.1	90.0	57.3
分解率(重量%)	32.0	53.1	22.2

[0039] With Catalyst A and the comparison catalyst B of this invention, to having attained high NP invert ratio and low cracking severity, even if other comparison catalysts C are high NP invert ratios, cracking severity is high, it has the fault that lubrication base oil fraction yield is low, and although Catalyst D is a 400-degree C elevated temperature, it has the fault that NP invert ratio is low.

[0040] Next, the following two examples show that the catalyst A of this invention is essentially excellent in wax isomerization ability compared with the comparison catalyst B.

[0041] (Example 2) The product obtained with the reaction temperature of 361 degrees C using the catalyst A of an example 1 was distilled under reduced pressure, the light part was removed, and the residue which has 330 degrees C of initial boiling points was obtained. Subsequently, this residue was dewaxed using the partially aromatic solvent of a methyl ethyl ketone/toluene (1 / 1 solvent ratio) on a solvent / dewaxing raw material ratios 4/1, and conditions with a temperature of -27 degrees C. The yield of the lubrication base oil obtained now and the description of this base oil were shown in Table 3.

[0042] (Example 4 of a comparison) In the example 1 of a comparison, lubrication base oil was obtained for the generation oil using Catalyst B by the same approach as an example 2. The oil yield in dewaxing processing and the description of base oil were shown in Table 3.

[0043]

[Table 3]

	実施例 2	比較例 4
基油収率(重量%)	66.8	24.6
基油性状		
流動点(℃)	-15.0	-12.5
動粘度(cSt, 100℃)	4.813	6.997
粘度指数	145	137

[0044] It is shown that Table 3 has the wax isomerization ability the catalyst A of this invention excelled [ability] in the essential target. That is, since the decomposition reaction to straight chain-like paraffin has priority and advances even if the comparison catalyst B has attained high NP invert ratio and low cracking severity in Table 2, the base oil of a viscosity index 145 is obtained with high dewaxed-oil yield from the product obtained from this invention catalyst A to only a product with the very low oil yield in the dewaxing processing which expresses extent of isomerization directly being obtained.



[0045]

[Effect of the Invention] It does so the effectiveness according to rank that it can be used also for general-purpose lubrication base oil manufacture while it can obtain the lubrication base oil which has a high viscosity index by high yield, since the wax isomerization catalyst of this invention shows the high rate of isomerization, and low cracking severity, without pretreating a raw material wax.

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TECHNICAL FIELD

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PRIOR ART

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[0008]

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EFFECT OF THE INVENTION

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[Effect of the Invention] It does so the effectiveness according to rank that it can be used also for general-purpose lubrication base oil manufacture while it can obtain the lubrication base oil which has a high viscosity index by high yield, since the wax isomerization catalyst of this invention shows the high rate of isomerization, and low cracking severity, without pretreating a raw material wax.

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[Translation done.]

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned technical problem, and the purpose of this invention can prepare it by the simple approach. The resistance over sulfur and nitrogen uses the high, high wax isomerization catalyst of versatility, and its catalyst. It is in providing the isomerization approach of a wax of obtaining the lubrication base oil which has a high viscosity index called 140 or more and the low pour point by high yield, and a list with the manufacture approach of lubrication base oil that purification of the usual lubricating oil raw material and manufacture of the lubricating oil of the hyperviscous characteristic from slack wax can be performed by turns.

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MEANS

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[Means for Solving the Problem] In order to advance isomerization promptly on the dual function nature catalyst which supported the metal on fireproof oxide support, it is supposed that metaled dehydrogenation and hydrogenation activity, and the acidity (acidity per surface area) of support must be raised with both sufficient balance. For example, if a zeolite is used as support in order to raise acidity, a decomposition reaction will have priority and the base oil of a low viscosity index will be obtained only with low yield. Alternative decomposition and alternative isomerization are performed or the approach using what raised the SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> ratio of a crystalline molecular sieve using the molecular sieve effect using the crystalline molecular sieve which has a specific pole diameter as a policy for controlling this decomposition activity, and made acidity low etc. is learned. Moreover, the noble metals which have a dehydrogenation and hydrogenation activity high as a support metal, especially platinum were found, and have been used in order to raise a dehydrogenation and hydrogenation activity. It is because it is supposed that this has indispensable noble-metals components, such as platinum, in the balance of metaled dehydrogenation and hydrogenation activity, and support acidity when a crystalline molecular sieve is made into a subject, and restricting is desirable as for use of base metal, such as nickel, (for example, ACS preprint 38(4) 788, 1993 reference).

[0010] However, the molecular sieve function was demonstrated enough, and having carried out little addition of the crystalline molecular sieve also unexpectedly at the alumina also found out that, as for the acidity, the acidity of a crystalline molecular sieve was reflected in the acidity of support as it is. And the support which added to the alumina the crystalline molecular sieve which has a specific pole diameter, and raised the SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> ratio more than fixed, and made acidity low Even if it supports 8 group base metal and 6A group metal which are used with general hydrorefining catalysts other than the metal which has very high hydrogenation ability like noble metals like palladium or platinum It found out that a dehydrogenation and hydrogenation activity, and the acidity of support balanced well, and isomerization of a wax advanced promptly.

[0011] This invention is what was made based on this knowledge. This invention to an alumina To the support which has pore with a major axis of 6.5-7.5Å, and mixed the crystalline molecular sieve whose SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>4</sub> mole ratio is 50 or more one to 30% of the weight Nickel, cobalt, molybdenum, the catalyst for wax isomerization that consists of having made at least one sort of metal components chosen from a tungsten support, And the isomerization approach of the wax which consists of contacting the wax system hydrocarbon oil which contains paraffin 50% of the weight or more for the aforementioned catalyst for wax isomerization under hydrogen pressurization, It is the manufacture approach of the lubrication base oil which consists of carrying out the run of lubrication base oil manufacture intermediate field and the slack wax to the reactor which filled up the list with said wax isomerization catalyst by turns, and performing hydrorefining of said lubrication base oil manufacture intermediate field, and isomerization of slack wax by turns.

[0012] Although hydrated alumina is included in the alumina used for above-mentioned this invention, if it is the alumina usually used as support of a catalyst, or hydrated alumina as this alumina, especially trouble does not have anythings and they can be used.

[0013] The crystalline molecular sieve used for this invention needs to be the crystalline molecular sieve whose pore major axis is 6.5-7.5Å. If a pore major axis is smaller than 6.5Å, only decomposition of straight chain-like paraffin and the small branching paraffin of extent of branching will advance, and isomerization will not advance. in this case, also although kicked, in order for components other than paraffin to make abundant \*\* rare \*\*\*\*\* and the so-called waxy distillate only form into the low pour point, when [ which used the wax as the raw material ] suitable, in the dewaxing processing performed succeedingly, the yield of lubrication base oil becomes remarkably low. On the other hand, if a pore major axis is larger than 7.5Å, a molecular sieve function will be substantially lost to a wax, and only the base oil of low lubrication base oil fraction yield and a low viscosity index will be obtained.

[0014] The silicoaluminophosphate molecular sieve (SAPO) which are Zeolites L, Y, and omega, mordenite, and the zeolite analogue is mentioned to the crystalline molecular sieve whose pore major axis is 6.5-7.5Å, and each of these can be used for it. However, although it has the pore whose pole diameter is 7.4Å, since Zeolite Y has the-like secondary decomposition resulting from the channel structure, it is not [ among these ] so desirable to wax isomerization.

[0015] Moreover, this crystalline molecular sieve needs to make acidity low, and uses what made the SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> mole ratio 50 or more for this reason. catalyst deactivation according [ if SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> mole ratio does not fulfill 50, even if it is little addition, decomposition activity will be too high and only the base oil of low lubrication base oil fraction yield and a low viscosity index will be obtained or ] to deposition of Cork etc. -- intense -- a catalyst life -- short -- \*\*\*\* -- \*\*

[0016] Although especially the configuration of a crystalline molecular sieve is not asked, it is desirable to use 100 micrometers or less of things which have the median size of 0.1-50 micrometers preferably. Moreover, the addition to the alumina of a crystalline molecular sieve is made into 1 - 30wt%. When not filling the addition of a crystalline molecular sieve to 1wt%, isomerization activity is low and the addition exceeding 30wt% is because decomposition activity becomes high and isomerization selectivity becomes low. Even if the molecular sieve function of a crystalline molecular sieve and acidity are little addition, they are enough demonstrated in this amount. moreover, the addition of the crystalline molecular sieve to an alumina is comparatively little in this way -- as a hydrogenation metal component -- the [ the 8th group base metal and ] -- use of 6A group metal is enabled.

[0017] the [ the 8th group base metal of a periodic table which is used for a general hydrotreating catalyst as a support metal and which is a hydrogenation metal component, and ] -- it uses combining any one sort, such as 6A group metal, for example, nickel, cobalt, molybdenum, and a tungsten, or two sorts or more. These amounts of metal support are good to be the total quantity as a metal component and to select suitably in 10 - 20% of the weight of the range especially preferably to a catalyst, three to 30% of the weight. When a crystalline molecular sieve like a zeolite as catalyst support was used, in order to have made the acidity, and the dehydrogenation and hydrogenation activity ability of a hydrogenation metal component balance well generally, it was thought that the noble metals which have high hydrogenation ability were required. However, in the support which carried out little addition of the crystalline molecular sieve with 1 - 30 % of the weight at the alumina, if the molecular sieve has suitable pore structure and acidity, the acidity as the whole support can be weakened moderately, consequently even if it is base metal, isomerization will advance promptly.

[0018] In addition, it may combine with these metal components and elements other than this, for example, Lynn etc., may be supported. Other elements, such as Lynn, are good to select suitably in 1 - 7% of the weight of the range.

[0019] The catalyst of this invention is the following, and can be made and prepared.

[0020] First, although an alumina and a crystalline molecular sieve are mixed and kneaded, even if this mixes both before kneading, kneading an alumina, it may add and mix and it may use a crystalline molecular sieve. it is not necessary to perform a special thing in this mixing, and it is only mixed mechanically -- being sufficient . In this kneading, it is desirable to use a nitric-acid solution as a deflocculant 1 to 5%. Moreover, which a well-known kneading machine can be used in kneading. After kneading is good to fabricate using an extruding press machine etc. As for the configuration in this case, it is desirable to fabricate in consideration of a cylinder form, 3 leaf shapes, and the reactor that it



spherical-\*\* and is used, and it is good to make it have the maximum cross-section diameter which are  $1/16 - 1/32$  inch.

[0021] next, this moldings -- the temperature of 50-200 degrees C -- 5 - 24 hours -- drying -- the temperature of 250-800 degrees C -- it is 400-700 degrees C in temperature preferably, and calcinates in 1 - 2-hour air. thus, the metal component described above by the sinking-in method etc. to the obtained fireproof oxide support -- supporting -- the temperature of 50-200 degrees C -- 5 - 24 hours -- drying -- the temperature of 250-700 degrees C -- it is 400-600 degrees C in temperature preferably, and calcinates in 0.5 - 2-hour air.

[0022] The catalyst of this invention obtained as mentioned above is suitably used, in order to isomerize the wax system hydrocarbon oil which contains paraffin 50% of the weight or more as a raw material. The slack wax which is missing from solvent dewaxing equipment and is obtained is used suitably, without carrying out furfural solvent extraction processing, and processing the deasphalting processing oil for quality, a heavy fraction, or reduced pressure residue with hydrorefining equipment subsequently among the slack wax obtained at the solvent dewaxing process which is one of the lubricating oil production processes, i.e., reduced pressure, or processing especially as a wax system hydrocarbon oil which contains this paraffin 50% of the weight or more, although that class is not asked. These waxes may be independently processed for every fraction, and it may mix with the thing of other fractions and they may be used.

[0023] It is desirable for any method of the fixed bed, the moving bed, and the fluid bed to be able to perform this isomerization, and to carry out by the reaction condition of the temperature which is 300-400 degrees C, the hydrogen pressure which is 50-150kg/cm<sup>2</sup>, the hydrogen / wax ratio of 500 - 3000 l/l, and the liquid space velocity (LHSV) of 0.2-5.0hr-1.

[0024] In order to obtain the lubrication base oil of a high viscosity index with high yield, it is desirable to set up a reaction condition so that the invert ratio to the light fraction in which the invert ratio of straight chain-like paraffin has the boiling point below the initial boiling point of a raw material 90% or more may become 40 or less % of the weight. When a straight chain-like paraffin invert ratio does not reach to 90%, although a high viscosity index is expectable, the yield of lubrication base oil may fall in the dewaxing processing performed succeedingly, and it may not be able to make low enough the pour point of the lubrication base oil concerned. Moreover, if the inversion to a light part exceeds 40 % of the weight, a high viscosity index cannot be maintained the top where the yield of a lubrication base oil fraction is low, and it is not desirable.

[0025] Since the light fraction which is not desirable as lubrication base oil is contained in the generation oil obtained by this isomerization, distillation etc. separates this. It is desirable to perform this distillation under reduced pressure, and it is good to obtain residue which removes the fraction of 350 degrees C or less of boiling points, and has the 330-370-degree C initial boiling point.

[0026] After distilling an isomerization product, it can consider as lubrication base oil by applying to dewaxing equipment. The solvent dewaxing currently generally performed is sufficient as dewaxing in this case, for example, it is good to be a solvent / dewaxing raw material ratio 2 / the range of 1 - 4/1, and to carry out under -20--30 degree C temperature using the partially aromatic solvent (for example, 1 / 1 solvent ratio) of a methyl ethyl ketone/toluene.

[0027] Since at least one sort chosen from the nickel which is the hydrogenation metal component which is used for a hydrorefining catalyst general as a support metal, cobalt, molybdenum, and a tungsten is used for the above-mentioned catalyst, it also has hydrorefining functions, such as desulfurization and denitrification, with isomerization. Therefore, the vacuum distillation fraction of mineral oil etc. can also carry out hydrorefining of the manufacture intermediate field of usual lubrication base oil using this catalyst. Therefore, conventionally, isomerization and hydrorefining are one reactor by using this catalyst, although the separate reactor was performing, and can perform isomerization by turns with hydrorefining, respectively by letting usual lubrication base oil manufacture intermediate field and a usual wax pass by turns.

[0028] these two or more sorts of mixture, such as a raffinate which the above-mentioned usual lubrication base oil manufacture intermediate field are intermediate field generally obtained by the

lubrication base oil production process, and carried out solvent refining of the propane deasphalting processing oil of a vacuum distillation fraction and the vacuum distillation residue, or these using the furfural typically and/or an oil which carried out solvent dewaxing, or an oil which carried out contact dewaxing, etc. -- it is -- a sulfur content -- about 0.5-5wt% -- it is desirable to use what is contained.

[0029] This hydrorefining is good under 50-150kg/cm<sup>2</sup> hydrogen pressurization to carry out to the bottom of a condition with the hydrogen / oil ratio of 100 - 2000 l/l, a liquid space velocity [ of 0.5-5hr-1 ] (LHSV), and a temperature of 250-400 degrees C.

[0030] Moreover, since the stock oil kind supplied to a reactor is changed, and conditions are reset up after that or conditions are reset up in case the above-mentioned hydrorefining and isomerization are performed by turns, you may carry out by which approach of changing a stock oil kind after that.

Although the lubrication base oil which has the target description isomerization from hydrorefining or since the activity of a catalyst is not fully demonstrated [ in / conversely / the early stages of the change to hydrorefining from isomerization ] cannot be obtained, activity can revive within a short period of time comparatively, and the lubrication base oil which has the target description can be obtained now.

[0031] In addition, although it is necessary to perform vacuum distillation in order for isomerization and the inversion to the light fraction by the decomposition reaction which is side reaction similarly to take place and for this hydrorefining to also remove the light fraction which is not desirable as this lubrication base oil, in hydrorefining and both of isomerization, a common fractionating tower can be used also about this distillation. Furthermore, although it may usually be applied to dewaxing equipment like [ after this hydrorefining ] the isomerization back, since this dewaxing condition does not have a difference so much in both, either, it can be used in common.

[0032] Moreover, although based also on the class of lubrication base oil manufacture intermediate field used in this hydrorefining, generally with a viscosity index of 120 or less lubrication base oil is obtained.

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[Translation done.]

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## EXAMPLE

[Example]

(Example 1)

1564g of preparation alumina powder of a catalyst was put into the kneading machine, nitric-acid water-solution 1 l of 3% concentration was added as a deflocculant, and it kneaded for 30 minutes, and mordenite (zeolite pore major-axis [ of 7.0A ], mole ratio of  $\text{SiO}_2/\text{aluminum } 2\text{O}_3 = 210$ ) 117.7g of marketing was added to this, and it kneaded for 30 more minutes to it. This kneading object was fabricated with the extruding press machine which has the dice of the hole of 1.4mmphi in the shape of a cylinder, and it dried at 130 degrees C overnight. The dry matter was calcinated at 600 degrees C for 1 hour using rotary kiln, and catalyst support was obtained.

[0034] Molybdenum, nickel, and Lynn were sunk in using the sinking-in liquid which contains 46.5g of ammonium molybdates, 41.8g of nickel nitrate 6 hydrates, and 19.6g of phosphoric-acid solutions in 150g of this support. After drying this at 130 degrees C overnight, it calcinated for 30 minutes at 500 degrees C using rotary kiln, and Catalyst A was acquired.

[0035] After filling up the reaction container of a fixed-bed circulation type with the catalyst A acquired by the isomerization above of a wax and sulfurating this catalyst, it isomerized by circulating the heavy slack wax (13 % of the weight of oil, consistency 0.84 g/cm<sup>3</sup>, 330-600 degrees C of boiling ranges) obtained by carrying out solvent dewaxing of the heavy lubrication fraction after vacuum distillation to this. The reaction condition set to 80kg/cm<sup>2</sup> of hydrogen pressure, hydrogen / wax ratio 1500 l/l, and LHSV 0.5hr<sup>-1</sup>, and temperature was changed among 350-380 degrees C. The gas chromatography analyzed the obtained generation oil and the result was shown in Table 1. In addition, NP invert ratio and the yield of a fraction with the boiling point lower than 330 degrees C were expressed for the percentage reduction of straight chain-like paraffin as cracking severity.

[0036]

[Table 1]

反応温度(℃)	3 5 0	3 6 1	3 6 5	3 7 0
NP転化率(%)	6 8 . 2	9 2 . 3	9 6 . 1	1 0 0
分解率(重量%)	1 4 . 0	3 2 . 3	4 4 . 8	6 7 . 6

[0037] (Examples 1-3 of a comparison)

It replaces with mordenite in an example 1, and is PQ. The zeolite beta (the zeolite pore major axis of 7.6A, the mole ratio of  $\text{SiO}_2/\text{aluminum } 2\text{O}_3 = 141$ ) which carried out dealuminization of Silicalite made from Zeolite (the zeolite pore major axis of 5.6A, the mole ratio of  $\text{SiO}_2/\text{aluminum } 2\text{O}_3 = 250$ ) and the commercial zeolite beta was used, respectively, and also Catalysts B and C were prepared by the same approach as an example 1. Moreover, Catalyst D was prepared by the same approach as an example 1 using the support of only an alumina, without adding mordenite. After sulfurating these catalysts, the isomerization experiment was conducted by the same approach as an example 1 except reaction temperature having been shown in Table 2. These results were shown in Table 2.

[0038]

[Table 2]

触媒	B	C	D
反応温度(℃)	335	337	400
NP転化率(%)	93.1	90.0	57.3
分解率(重量%)	32.0	53.1	22.2

[0039] With Catalyst A and the comparison catalyst B of this invention, to having attained high NP invert ratio and low cracking severity, even if other comparison catalysts C are high NP invert ratios, cracking severity is high, it has the fault that lubrication base oil fraction yield is low, and although Catalyst D is a 400-degree C elevated temperature, it has the fault that NP invert ratio is low.

[0040] Next, the following two examples show that the catalyst A of this invention is essentially excellent in wax isomerization ability compared with the comparison catalyst B.

[0041] (Example 2) The product obtained with the reaction temperature of 361 degrees C using the catalyst A of an example 1 was distilled under reduced pressure, the light part was removed, and the residue which has 330 degrees C of initial boiling points was obtained. Subsequently, this residue was dewaxed using the partially aromatic solvent of a methyl ethyl ketone/toluene (1 / 1 solvent ratio) on a solvent / dewaxing raw material ratios 4/1, and conditions with a temperature of -27 degrees C. The yield of the lubrication base oil obtained now and the description of this base oil were shown in Table 3.

[0042] (Example 4 of a comparison) In the example 1 of a comparison, lubrication base oil was obtained for the generation oil using Catalyst B by the same approach as an example 2. The oil yield in dewaxing processing and the description of base oil were shown in Table 3.

[0043]

[Table 3]

	実施例 2	比較例 4
基油収率(重量%)	66.8	24.6
基油性状		
流動点(℃)	-15.0	-12.5
動粘度(cSt, 100℃)	4.813	6.997
粘度指数	145	137

[0044] It is shown that Table 3 has the wax isomerization ability the catalyst A of this invention excelled [ ability ] in the essential target. That is, since the decomposition reaction to straight chain-like paraffin has priority and advances even if the comparison catalyst B has attained high NP invert ratio and low cracking severity in Table 2, the base oil of a viscosity index 145 is obtained with high dewaxed-oil yield from the product obtained from this invention catalyst A to only a product with the very low oil yield in the dewaxing processing which expresses extent of isomerization directly being obtained.

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(54) 【発明の名称】 ワックス異性化用触媒およびワックスの異性化方法並びに潤滑基油の製造方法

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(57) 【特許請求の範囲】

【請求項1】 アルミナに、長径6.5～7.5Åの細孔を有し、かつSiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>モル比が50以上である結晶性モレキュラーシーブを1～30重量%混合した担体に、ニッケル、コバルト、モリブデン、タングステンから選択される少なくとも1種の金属成分を担持させたことからなるワックス異性化用触媒。

【請求項2】 請求項1に記載の結晶性モレキュラーシーブが、ゼオライトL、ゼオライトQ、モルデナイトまたはシリコアルミノホスフェート・モレキュラーシーブから選ばれた少なくとも1つであることを特徴とするワックス異性化用触媒。

【請求項3】 パラフィンを含む50重量%以上含有するワックス系炭化水素油を水素加圧下に請求項1に記載のワックス異性化用触媒と接触させることを特徴とするワ

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ックスの異性化方法。

【請求項4】 請求項3に記載のワックス系炭化水素油がスラックワックスであることを特徴とするワックスの異性化方法。

【請求項5】 請求項1に記載のワックス異性化触媒を充填した反応器に潤滑基油製造中間体とスラックワックスとを交互に通油して、前記潤滑基油製造中間体の水素化精製とスラックワックスの異性化とを交互に行うことを特徴とする潤滑基油の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、ワックス系炭化水素油、特にスラックワックスを異性化し、高い粘度指数を有する潤滑基油を製造するのに適した触媒、およびその触媒を用いたワックスの異性化方法、さらには潤滑基油

の製造方法に関する。

【0002】

【従来の技術】スラックワックスを異性化したり、選択的な水素化分解を行うことによって、粘度指数の高い潤滑基油を製造することができ、このための方法あるいは触媒等について種々提案されている。このうち、高い粘度指数を有する潤滑油の製造方法として、耐火性酸化物、具体的にはアルミナを担体とし、これにニッケルおよび／またはコバルトと、モリブデンおよび／またはタングステンとリン酸化物を担持した触媒を用いる方法が

提案されている（特公昭54-2204号公報）。しかし、この触媒を用いる方法では、異性化の反応率が低く、低い潤滑基油収率しか得られないという欠点があった。

【0003】このため、反応率を高め、潤滑基油の収率を向上させるため、種々の触媒を用いる方法が提案されている。

【0004】例えば、大気孔ゼオライト（ZSM-5、22、23、35）あるいはアルファ値が20を越えない低酸性ゼオライト（骨格にホウ素を含むゼオライトβ）上に、パラジウム、白金等の水素化／脱水素成分を担持した触媒（特開昭62-112691号公報、特開平5-504597号公報、特開平4-226593号公報）、中間的気孔孔径をもつシリコアルミノホスフェート・モレキュラーシーブに白金やパラジウムを担持した触媒（特開昭62-25195号公報、特開平4-503371号公報）等が提示されている。

【0005】また、フッ素化された耐火金属酸化物担体に白金等を担持した触媒（特開平1-223196号公報）、テトラアンモニウムアルミネート等で処理した耐火金属酸化物担体に白金等を担持した触媒（特開昭60-133089号公報）が開示されている。

【0006】しかし、この種の触媒を用いて得られる潤滑基油は、流動点あるいは粘度指数等の面で省燃費型モーターオイルとして使用するにはいまだ十分ではない場合もあり、さらにはこれらの触媒のほとんどは、硫黄、窒素に対する耐性の低い貴金属が活性担持金属として使用されており、原料中の硫黄、窒素分を厳密に制御しなければならないという欠点を有していた。従って、これら貴金属が担持された触媒を用いてワックス等を異性化して高い粘度指数を有する基油を製造するには、脱硫、脱窒素のための別の反応器が必要となる。

【0007】さらに、ゼオライトやシリコアルミノホスフェート・モレキュラーシーブ等を用いた触媒は、アルミナ担体触媒と比べ高価であるという欠点を有している。また、耐火金属酸化物担体をフッ素やテトラアンモニウムアルミネート等で処理したものは、触媒の製造工程が複雑になり、またフッ素等有害な試薬を用いるため、製造上の安全性確保等の問題もあった。

【0008】

【発明が解決しようとする課題】本発明は、上記課題を解決するもので、本発明の目的は簡便な方法で調製でき、硫黄、窒素に対する耐性が高く汎用性の高いワックス異性化触媒、およびその触媒を用いて、140以上という高い粘度指数と低い流動点を有する潤滑基油を高収率で得るワックスの異性化方法、並びに通常の潤滑油原料の精製とスラックワックスからの高粘度指数の潤滑油の製造とを交互に行うことができる潤滑基油の製造方法を提供することにある。

【0009】

【課題を解決するための手段】耐火性酸化物担体上に金属を担持した二元機能性触媒上で異性化を速やかに進行させるためには、金属の脱水素・水素化活性と担体の酸性度（表面積当たりの酸量）をとともにバランスよく高めなければならないとされている。例えば、酸性度を高める目的で担体としてゼオライトを用いると分解反応が優先し、低い粘度指数の基油が低い収率でしか得られない。この分解活性を抑制するための方策として、特定の細孔径を有する結晶性モレキュラーシーブを用いて分子ふるい効果を利用して選択的な分解や異性化を行った

り、あるいは結晶性モレキュラーシーブの $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比を高めて酸性度を低くしたものをを用いる方法などが知られている。また、脱水素・水素化活性を高める目的で、担持金属としては高い脱水素・水素化活性を有する貴金属、特に白金が好んで用いられてきた。これは結晶性モレキュラーシーブを主体とした場合には、金属の脱水素・水素化活性と担体酸性度とのバランスにおいて、白金等の貴金属成分が必須であり、ニッケルなどの卑金属の使用は制限することが好ましいとされているためである（例えば、ACS preprint 38(4)788,1993参照）。

【0010】しかし、意外にも結晶性モレキュラーシーブはアルミナに少量添加しただけでも、その分子ふるい機能は充分発揮され、またその酸性度は、結晶性モレキュラーシーブの酸性度がそのまま担体の酸性度に反映されることを見出した。しかも、特定の細孔径を有し、かつ $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比を一定以上に高めて酸性度を低くした結晶性モレキュラーシーブをアルミナへ添加した担体は、パラジウムや白金のような貴金属のような極めて高い水素化能を有する金属以外の、一般の水素化精製触媒で用いられるような8族卑金属、6A族金属を担持しても、脱水素・水素化活性と担体の酸性度とがうまくバランスして、ワックスの異性化が速やかに進行することを見いだした。

【0011】本発明はかかる知見に基づきなされたもので、本発明はアルミナに、長径6.5～7.5Åの細孔を有し、かつ $\text{SiO}_2/\text{Al}_2\text{O}_3$ モル比が50以上である結晶性モレキュラーシーブを1～30重量%混合した担体に、ニッケル、コバルト、モリブデン、タングステンから選択される少なくとも1種の金属成分を担持させたこと

50重量%以上含有するワックス系炭化水素油を水素加圧下に前記のワックス異性化用触媒と接触させることとなるワックスの異性化方法、並びに前記ワックス異性化触媒を充填した反応器に潤滑基油製造中間体とスラックワックスとを交互に通油して、前記潤滑基油製造中間体の水素化精製とスラックワックスの異性化とを交互に行うこととなる潤滑基油の製造方法である。

【0012】上記本発明に用いられるアルミナにはアルミナ水和物を含むが、このアルミナとしては、触媒の担体として通常用いられるアルミナ、あるいはアルミナ水和物であればどのようなものでも特に支障はなく用いることができる。

【0013】本発明に用いられる結晶性モレキュラーシーブは、細孔長径が6.5～7.5 Åである結晶性モレキュラーシーブであることが必要である。細孔長径が6.5 Åより小さいと、直鎖状パラフィン及び分岐の程度の小さい枝分かれパラフィンの分解のみが進行し、異性化反応が進行しない。この場合、パラフィン以外の成分が多量含まれている、いわゆる含ろう油を、単に低流動点化させるためには適しているけれども、ワックスを原料とした場合には、引き続いて行われる脱ろう処理において、潤滑基油の収率が著しく低くなる。一方、細孔長径が7.5 Åより大きいと、ワックスに対して実質的に分子ふるい機能が失われ、低い潤滑基油留分収率、低い粘度指数の基油しか得られない。

【0014】細孔長径が6.5～7.5 Åである結晶性モレキュラーシーブには、ゼオライトL、Y、 $\Omega$ 、モルデナイト、ゼオライト類似化合物であるシリコアルミノホスフェート・モレキュラーシーブ(SAPO)が挙げられ、これらはいずれも用いることができる。しかし、このうち、ゼオライトYは、細孔径が7.4 Åの細孔を有しているが、そのチャンネル構造に起因した2次的な分解があるのでワックス異性化にはあまり好ましくない。

【0015】また、この結晶性モレキュラーシーブは酸性度を低くしたものである必要があり、このため $\text{SiO}_2/\text{Al}_2\text{O}_3$ モル比を50以上としたものを用いる。 $\text{SiO}_2/\text{Al}_2\text{O}_3$ モル比が50に満たないと、少量の添加であっても分解活性が高すぎて低い潤滑基油留分収率、低い粘度指数の基油しか得られないか、またコーク等の堆積による触媒失活が激しく触媒寿命が短くなる。

【0016】結晶性モレキュラーシーブの形状は特に問わないが、100  $\mu\text{m}$ 以下、好ましくは0.1～50  $\mu\text{m}$ のメジアン径を有するものを使用することが好ましい。また、結晶性モレキュラーシーブのアルミナへの添加量は1～30 wt%とする。結晶性モレキュラーシーブの添加量が1 wt%に満たない場合は、異性化活性が低く、また、30 wt%を越える添加は、分解活性が高くなり、異性化選択性が低くなるためである。結晶性モレキュラーシーブの分子ふるい機能や、酸性度は少量の添加であっても、この量で充分発揮される。また、このように、ア

ルミナへの結晶性モレキュラーシーブの添加量が比較的少量であることが水素化金属成分として第8族卑金属及び第6A族金属の使用を可能にする。

【0017】担持金属としては、一般の水素化精製触媒に用いられるような水素化金属成分である周期律表第8族卑金属及び第6A族金属、例えばニッケル、コバルト、モリブデン及びタングステン等のいずれか1種あるいは2種以上を組み合わせて用いる。これらの金属担持量は、触媒に対し、金属成分としての合計量で、好ましくは3～30重量%、特には10～20重量%の範囲で適宜選定するとよい。一般的に、触媒担体としてゼオライトのような結晶性モレキュラーシーブを用いる場合、その酸性度と水素化金属成分の脱水素・水素化活性能とをうまくバランスさせるには、高い水素化能を有する貴金属が必要であると考えられていた。しかし、結晶性モレキュラーシーブをアルミナに1～30重量%と少量添加した担体では、モレキュラーシーブが適切な細孔構造と酸性度を有していれば、担体全体としての酸性度は適度に弱められ、その結果、卑金属であっても異性化が速やかに進行するのである。

【0018】なお、これらの金属成分に併せて、これ以外の元素、例えばリン等を担持してもよい。リン等の他の元素は1～7重量%の範囲で適宜選定するとよい。

【0019】本発明の触媒は、以下のようにして調製できる。

【0020】まず、アルミナと結晶性モレキュラーシーブとを混合、混練するが、これは混練前に両者を混合しても、アルミナを混練しながら結晶性モレキュラーシーブを添加、混合して用いても良い。この混合には、特別のことを行なう必要はなく、単に機械的に混合させるだけで良い。この混練においては、1～5%硝酸溶液を解膠剤として使用することが好ましい。また、混練においては公知の何れの混練機を使用できる。混練後は、押出成形機等を用いて成形すると良い。この場合の形状は、シリンダー形、三つ葉形、球状等、使用する反応器を考慮して成形することが好ましく、1/16～1/32インチの最大断面直径を有するようにすると良い。

【0021】次にこの成形物を50～200℃の温度で、5～24時間乾燥し、250～800℃の温度、好ましくは400～700℃の温度で、1～2時間空气中で焼成する。このようにして得られた耐火性酸化物担体に、含浸法等により上記した金属成分を担持し、50～200℃の温度で、5～24時間乾燥し、250～700℃の温度、好ましくは400～600℃の温度で、0.5～2時間空气中で焼成する。

【0022】上記のようにして得られる本発明の触媒はパラフィンを50重量%以上含有するワックス系炭化水素油を原料として異性化するために好適に用いられる。このパラフィンを50重量%以上含有するワックス系炭化水素油としては、特にはその種類を問わないが、潤滑



油製造工程の1つである溶剤脱ろう工程で得られるスラックワックス、すなわち、減圧中質、重質留分もしくは減圧残渣分の脱アスファルト処理油を、フルフルール溶剤抽出処理し、次いで水素化精製装置で処理するか、もしくは処理することなく、溶剤脱ろう装置にかけて得られるスラックワックスが好適に用いられる。これらのワックスは、各留分ごとに単独で処理しても良く、また他の留分のものと混合して用いても良い。

【0023】この異性化は、固定床、移動床、流動床の何れの方式でも行なうことができ、300～400℃の温度、50～150 kg/cm<sup>2</sup>の水素圧、500～3000 l/lの水素/ワックス比、0.2～5.0 hr<sup>-1</sup>の液空間速度(LHSV)の反応条件で行なうことが好ましい。

【0024】高い粘度指数の潤滑基油を高い収率で得るためには、直鎖状のパラフィンの転化率が90%以上、原料の初留点以下の沸点を有する軽質留分への転化率が40重量%以下になるように反応条件を設定することが好ましい。直鎖状のパラフィン転化率が90%に達しない場合、高い粘度指数は期待できるが、引き続き行う脱ろう処理において潤滑基油の収率が低下し、また、当該潤滑基油の流動点を十分に低くできない場合がある。また、軽質分への転化が40重量%を越えると、潤滑基油留分の収率が低い上、高い粘度指数が維持できず、好ましくない。

【0025】この異性化反応で得られた生成油には、潤滑基油としては望ましくない軽質留分が含まれるので、これを蒸留などにより分離する。この蒸留は減圧下で行なうことが望ましく、沸点350℃以下の留分を除去し、330～370℃の初留点を有する残留分を得るようにすると良い。

【0026】異性化生成物を蒸留した後、脱ろう装置にかけることにより、潤滑基油とすることができ。この場合の脱ろうは一般に行なわれている溶剤脱ろうで良く、例えば、メチルエチルケトン/トルエンの混合溶剤(例えば1/1溶剤比)を用い、溶剤/脱ろう原料比2/1～4/1の範囲で、-20～-30℃の温度の下で行なうと良い。

【0027】上記触媒は、担持金属として一般の水素化精製触媒に用いられるような水素化金属成分であるニッケル、コバルト、モリブデン、タングステンから選択される少なくとも1種を用いているので、異性化とともに、脱硫、脱窒素等の水素化精製機能をも有している。したがって、本触媒を用いて、鉱油の減圧蒸留留分等、通常の潤滑基油の製造中間体を水素化精製することでもできる。したがって、従来、異性化と水素化精製とは別々の反応装置で行っていたが、この触媒を用いることにより1つの反応装置で、通常の潤滑基油製造中間体とワックスとを交互に通すことにより水素化精製と異性化をそれぞれ交互に行うことができる。

【0028】上記の通常の潤滑基油製造中間体とは、一

般に潤滑基油製造工程で得られる中間体であり、典型的には減圧蒸留留分や、減圧蒸留残分のプロパン脱アスファルト処理油、或いはこれらを、フルフルールを用いて溶剤精製したラフィネートおよび/または溶剤脱ろうした油または接触脱ろうした油等、あるいはこれらの2種以上の混合物等であり、硫黄分を0.5～5 wt%程度含有しているものを用いることが好ましい。

【0029】この水素化精製は、50～150 kg/cm<sup>2</sup>の水素加圧下で、100～2000 l/lの水素/油比、0.5～5 hr<sup>-1</sup>の液空間速度(LHSV)、250～400℃の温度の条件下に行うと良い。

【0030】また、上記水素化精製と異性化とを交互に行う際には、反応器に供給される原料油種を切り替え、その後条件を設定し直すか、条件を設定し直してから、その後原料油種を切り替えるいずれの方法で行なっても良い。水素化精製から異性化、或いは逆に異性化から水素化精製への切り替えの初期においては、触媒の活性が十分に発揮されないため目的の性状を有する潤滑基油を得ることができないが、比較的短期間のうちに活性が復活し、目的の性状を有する潤滑基油を得ることができるようになる。

【0031】尚、この水素化精製でも、異性化と同様に副反応である分解反応による軽質留分への転化が起こり、この潤滑基油として望ましくない軽質留分を除去するため、減圧蒸留を行なう必要があるが、この蒸留についても水素化精製及び異性化の両者において共通の精留塔を使用できる。さらに、通常、この水素化精製後も異性化後と同様脱ろう装置にかけられる場合があるが、この脱ろう条件も両者においてさほど違いがないため共通して使用できる。

【0032】また、この水素化精製においては用いられる潤滑基油製造中間体の種類にもよるが、一般には粘度指数120以下の潤滑基油がえられる。

【0033】

【実施例】

(実施例1)

触媒の調製

アルミナ粉1564 gを混練機に入れ、3%濃度の硝酸水溶液1 lを解膠剤として添加して30分間混練し、これに市販のモルデナイト(ゼオライト細孔孔径7.0 Å、SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>のモル比=210)117.7 gを添加し、さらに30分間混練した。この混練物を1.4 mmφの孔のダイスを有する押出成形機で円柱状に成形し、130℃で一晩乾燥した。乾燥物をロータリーキルンを用いて600℃で1時間焼成し、触媒担体を得た。

【0034】この担体150 gに、モリブデン酸アンモニウム46.5 g、硝酸ニッケル六水和物41.8 g、リン酸溶液19.6 gを含む含浸液を用いてモリブデン、ニッケル、リンを含浸した。これを130℃で一晩乾燥した後、ロータリーキルンを用いて500℃で30分間焼成

して触媒Aを得た。

#### 【0035】ワックスの異性化

上記で得た触媒Aを固定床流通式の反応容器に充填し、この触媒を硫化した後、これに、減圧蒸留後の重質潤滑留分を溶剤脱ろうすることによって得られた重質スラックワックス（油分13重量%、密度0.84g/cm<sup>3</sup>、沸点範囲330～600℃）を流通させて異性化を行なった。反応条件は、水素圧80kg/cm<sup>2</sup>、水素／ワックス比\*

\*1500l/l、LHSV0.5hr<sup>-1</sup>とし、温度は350～380℃の間で変化させた。得られた生成油をガスクロマトグラフィーにより分析し、その結果を表1に示した。なお、直鎖状パラフィンの減少率をNP転化率、沸点が330℃より低い留分の生成率を分解率として表わした。

#### 【0036】

【表1】

反応温度(℃)	350	361	365	370
NP転化率(%)	68.2	92.3	96.1	100
分解率(重量%)	14.0	32.3	44.8	67.6

#### 【0037】（比較例1～3）

実施例1において、モルデナイトに代えてPQ Zeo Lite社製シリカライト（ゼオライト細孔長径5.6Å、SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>のモル比=250）、及び市販のゼオライトβを脱アルミしたゼオライトβ（ゼオライト細孔長径7.6Å、SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>のモル比=141）をそれぞれ用いた他は実施例1と同一の方法で触媒B、Cを調製した。また、モルデナイトを加えることなくアルミナのみを担体を用いて実施例1と同一の方法で触媒Dを調製した。これらの触媒を硫化した後、反応温度を表2に示したようにした以外は実施例1と同一の方法で異性化実験を行なった。これらの結果を表2に示した。

#### 【0038】

【表2】

触 媒	B	C	D
反応温度(℃)	335	337	400
NP転化率(%)	93.1	90.0	57.3
分解率(重量%)	32.0	53.1	22.2

【0039】本発明の触媒Aおよび比較触媒Bでは、高いNP転化率、低い分解率を達成しているのに対し、他の比較触媒Cは高いNP転化率であっても分解率が高く、潤滑基油留分収率が低いといった欠点を有しており、また、触媒Dは400℃の高温であるにもかかわらずNP転化率が低いといった欠点を有している。

【0040】次に、本発明の触媒Aが、比較触媒Bに比べて本質的にワックス異性化能に優れていることを次の二つの例で示す。

【0041】（実施例2）実施例1の触媒Aを用い反応温度361℃で得られた生成物を、減圧下で蒸留して軽質分を除去し、初留点330℃を有する残留物を得た。次いで、この残留物を、メチルエチルケトン／トルエン

（1/1溶剤比）の混合溶剤を用い、溶剤／脱ろう原料比4/1、温度-27℃の条件で脱ろうした。これ得られた潤滑基油の収率とこの基油の性状を表3に示した。

【0042】（比較例4）比較例1において、触媒Bを用いた生成油を、実施例2と同一の方法で潤滑基油を得た。脱ろう処理での油分収率と基油の性状を表3に示した。

#### 【0043】

【表3】

	実施例2	比較例4
基油収率(重量%)	66.8	24.6
基油性状		
流動点(℃)	-15.0	-12.5
動粘度(cSt, 100℃)	4.813	6.997
粘度指数	145	137

【0044】表3は、本発明の触媒Aが本質的に優れたワックス異性化能を有することを示している。すなわち、比較触媒Bは、表2で高いNP転化率、低い分解率を達成していても、直鎖状パラフィンに対する分解反応が優先して進行するため、異性化の程度を直接表わす脱ろう処理での油分収率が極めて低い生成物しか得られないのに対し、本発明触媒Aより得られた生成物からは、高い脱ろう油収率で粘度指数145の基油が得られている。

#### 【0045】

【発明の効果】本発明のワックス異性化触媒は、原料ワックスの前処理をすることなく高い異性化率と低い分解率を示すので高い粘度指数を有する潤滑基油を高収率で得ることができると共に、汎用潤滑基油製造にも使用することができるという格別の効果を奏するものである。